



RESEARCH MEMORANDUM

EXPLOSION AND COMBUSTION PROPERTIES OF ALKYL-SILANES

I - TEMPERATURE-COMPOSITION LIMITS OF EXPLOSION FOR

METHYL-, DIMETHYL-, TRIMETHYL-, TETRAMETHYL-, AND

VINYLSILANE AT ATMOSPHERIC PRESSURE

By Rose L. Schalla and Glen E. McDonald

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
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SUMMARY

The explosion limits of five alkylsilanes were determined as a function of temperature and composition at a pressure of 1 atmosphere. Over a fuel concentration range of 2 to 10 percent, the lowest temperatures ($^{\circ}\text{C}$) below which explosion did not occur for the five fuels studied were: tetramethylsilane $(\text{CH}_3)_4\text{Si}$, 450° ; trimethylsilane $(\text{CH}_3)_3\text{SiH}$, 310° ; dimethylsilane $(\text{CH}_3)_2\text{SiH}_2$, 220° ; methylsilane CH_3SiH_3 , 130° ; and vinylsilane $\text{H}_2\text{C}=\text{CH}-\text{SiH}_3$, 90° . Explosion limits for hydrocarbons analogous to these silanes fall in a temperature range of 500° to 600°C . Since the explosion temperatures of the alkylsilanes are lower than those of the hydrocarbons and since they decrease as hydrogen atoms are substituted for methyl groups, it was concluded that the Si-H bond is more readily susceptible to oxidation than the C-H bond.

INTRODUCTION

Combustion properties of hydrocarbon fuels such as flame speed, flammability limit, ignition energy, and quenching distance have been extensively investigated. For certain combustion processes, it is desirable to employ fuels which have more favorable combustion characteristics than the hydrocarbons, but which possess similar physical properties. A class of compounds which might meet these requirements is the alkylsilanes. Consequently, several alkylsilanes were prepared at the NACA Lewis laboratory; their physical properties (such as boiling point, melting point, heat of combustion, etc.) are reported in reference 1. At the time these alkylsilanes were synthesized, the conditions under which they could be safely handled and stored, particularly in contact with air, were not known. The present report describes a study directed toward establishing the conditions of temperature and concentration which will permit safe handling of this class of fuels.

Methyl-, dimethyl-, trimethyl-, tetramethyl-, and vinylsilane were investigated in this study. Premixed fuel-air mixtures, with the silane concentration ranging from about 2 to 10 percent by volume, were admitted to a heated, evacuated reaction vessel to a pressure of 1 atmosphere; and the lowest temperature at which explosion would occur was determined. The explosion region of these five alkylsilanes as a function of temperature and fuel-air composition was therefore established. A comparison of the explosion region of the alkylsilanes with the hydrocarbon compound which would result by replacing the silicon atom with a carbon atom was made wherever possible.

APPARATUS AND PROCEDURE

Fuels. - The method of preparing the alkylsilanes used in this study is described in reference 1. The tetramethylsilane had been purified from a commercially available product while the methyl-, dimethyl-, trimethyl-, and vinylsilanes had been prepared by reduction of the proper alkylchlorosilane with lithium aluminum hydride in anhydrous ethyl ether or dioxane.

Procedure. - A diagram of the apparatus used for determining the explosion limits of the alkylsilanes is shown in figure 1. Fuel and filtered air were admitted at the positions indicated and mixed in a 1-liter storage bulb by means of a magnetic stirrer. The pressure of the mixture in the storage bulb was such that, when opened to the heated, evacuated reaction vessel, the resulting pressure was 1 atmosphere. The temperature of the pyrex reaction vessel, $1\frac{1}{2}$ inches in diameter and $10\frac{1}{2}$ inches in length, was measured by a thermocouple attached to the outside of the vessel. The relatively large diameter of the reaction vessel was selected to minimize quenching effects.

Admission to the reaction vessel was usually made as rapidly as possible although, as described later, the mixture was sometimes admitted very slowly to determine the presence of cool flames. Occurrence of an explosion was indicated by a strong surge of the mercury in the manometer, and occasionally a flame was seen to travel up the tube leading from the reaction vessel. Although such flames usually did not travel very far, they did on several occasions flash back into the mixing bulb and cause a serious explosion in the line. Consequently, a roll of wire gauze was placed between the mixing bulb and the reaction vessel to serve as a flame trap. After this flame arrester was installed, no further trouble was encountered.

The minimum temperature for explosion was determined for various fuel-air mixtures of each given fuel. These minimum temperatures define the region of explosion and nonexplosion with respect to temperature and composition.

RESULTS

Tetramethyl- and Trimethylsilanes

Two distinctly different types of explosion limits were encountered in studying the silanes. The first type, typical of those reported for hydrocarbons at a pressure of 1 atmosphere, was found in this investigation for tetramethyl- and trimethylsilane. For both tetramethyl- and trimethylsilane, the fuel-air mixture was admitted rapidly to the evacuated reaction vessel to a pressure of 1 atmosphere, and at a sufficiently high temperature an explosion occurred. The explosion usually occurred within 30 seconds after admission. If no rapid reaction took place in this length of time, only a very slow increase in the pressure was observed and no explosion was later detected even after time intervals of 1 hour. It was observed for trimethylsilane that at certain temperatures below the explosion region, a pressure decrease would occur immediately after admission of the fuel-air mixture.

The temperature-composition curves for these two fuels are shown in figure 2. Determinations were made of both the temperature at which explosion occurred in 15 seconds or less and the temperature below which no explosion occurred. As shown in figure 2, these two temperatures do not differ by more than 15° C; and, consequently, the minimum explosion temperature must lie somewhere within this 15° C temperature range. Rich mixtures of tetramethylsilane and air ignited at a temperature as low as 450° C, while rich trimethylsilane-air mixtures required a temperature of only 310° C.

In figure 3 are presented the temperature-composition explosion curves for several hydrocarbon compounds as given in references 2 to 5. The boundary between explosion and nonexplosion for the hydrocarbons is between 500° and 600° C. The temperature-composition explosion curves for tetramethyl- and trimethylsilane are very similar to those of the hydrocarbons, except that the tetramethylsilane temperatures are about 100° C lower and the trimethylsilane temperatures are about 200° C lower than those of the hydrocarbons.

The temperature-composition explosion curves for representative hydrocarbons as shown in figure 3 lie in a narrow temperature range, while a marked separation is shown in figure 2 to exist between tetramethyl- and trimethylsilane. The apparent higher reactivity of trimethylsilane indicates that structural changes within the alkylsilanes may make marked differences in their combustion properties.

One reaction bulb was used throughout the determinations of the tetramethyl- and trimethylsilane explosion limits. During the course of these explosions small amounts of SiO₂ precipitated out on the walls of

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the reaction chamber. The reaction vessel was therefore replaced by a clean chamber, and a point on the trimethylsilane curve was redetermined. The explosion temperature obtained with the clean vessel was identical with that previously determined; and, consequently, the possibility that small amounts of SiO_2 were inhibiting or promoting the explosion was eliminated.

Dimethyl-, Methyl-, and Vinylsilanes

A second type of explosion limit was encountered with the dimethyl-, methyl-, and vinylsilanes; and the temperature-composition curves for these three compounds could not be obtained by the technique used for tetramethyl- and trimethylsilane. The temperatures below which no explosion occurred (reported in fig. 4) serve to indicate the temperature region for safe handling of a given fuel concentration. However, once temperatures above the nonexplosion region were reached, an explosion always took place before the mixtures reached a pressure of 1 atmosphere in the reaction vessel. Mixtures were therefore admitted very slowly to observe at what pressure the first indication of reaction did occur. By this procedure it was observed that a series of minor explosions, probably cool flames, occurred over a pressure range of 5 to 10 centimeters of mercury. After this pressure range was exceeded, no further reaction took place when the mixture was slowly admitted to a pressure of 1 atmosphere at temperatures just above the nonexplosion region.

Since a very vigorous reaction took place when the mixture was rapidly admitted, it is believed that the cool-flame reaction occurring at a pressure of 5 to 10 centimeters set off an explosive reaction when additional material was being rapidly supplied. The temperature-composition explosion curves for dimethyl-, methyl-, and vinylsilane actually represent the appearance of cool flames. The cool flames are capable of causing a true explosion if additional fuel-air mixture is immediately available to react. If cool flames did not occur, the explosion temperature for an air mixture of these fuels at an initial pressure of 1 atmosphere would be expected to be higher than the temperatures recorded here for these compounds.

DISCUSSION

A comparison of the explosion temperatures of the alkylsilanes with hydrocarbon fuels (see fig. 3) shows the marked decrease of the non-explosive region for the silanes as compared with that of typical hydrocarbons which would be formed if the silicon atoms were replaced by carbon. As already pointed out, the explosion curves of the hydrocarbons show little variation with changes in fuel structure. The explosion curves of tetramethyl-, trimethyl-, dimethyl-, and methylsilane are each separated from the next member of the series by about 100°C . The

3127 reactivity is obviously increased by substituting hydrogen atoms for the methyl groups. Since the explosion temperature is lower for the alkylsilanes than for the hydrocarbons and since it decreases as hydrogen atoms are substituted for methyl groups, it appears very probable that the Si-H bond is more readily subject to oxidation than the C-H bond. This conclusion might also have been reached by considering the theoretical bond-strength calculations of Pauling (ref. 6) which show the strength of the Si-H bond to be appreciably weaker than that of the C-H bond. Bond length measurements by Brockway and Beach (ref. 7) also show the Si-H bond to be considerably longer and therefore weaker than the C-H bond.

Walsh (ref. 8) has proposed that oxidation reactions of the hydrocarbons proceed by free radicals. To permit the formation of these radicals the first step in the oxidation must involve the vulnerability of the molecule to bond-breaking reactions. Walsh proposes that radicals are first formed by removal of a hydrogen atom from the molecule, which is then subject to attack by addition of O_2 to the free carbon valence. A general over-all scheme starting with a free radical R can therefore be presented as follows (ref. 9):



The fact that the alkylsilanes oxidize more readily than the hydrocarbons, and that hydrogen atoms can be removed more readily from the silanes, would lend support to the initial step proposed for the hydrocarbon oxidation mechanism, namely, the removal of a hydrogen atom. If the silane oxidation then follows the mechanism of the hydrocarbon oxidation, the scheme presented in equation (1) might also be adopted.

Since the explosion curve for vinylsilane is about $130^\circ C$ lower than for dimethylsilane, the $H_2C=CH$ group appears to introduce appreciably more reactivity into the molecule than does the C_2H_5 radical. However, even mixtures of vinylsilane vapor and air are nonexplosive below $90^\circ C$; thus, the most reactive fuel studied can be safely handled at room temperature without danger of a purely spontaneous reaction. Spontaneous combustion which might result when a large volume of a liquid silane fuel is exposed to air for long time periods was not studied in this research.

SUMMARY OF RESULTS

In an investigation of the nonexplosive region of five alkylsilanes as a function of temperature and concentration at a pressure of 1 atmosphere, the following results were obtained:

1. Over a fuel concentration range of 2 to 10 percent, the lowest temperatures ($^{\circ}\text{C}$) below which explosion did not occur for the five fuels studied were tetramethylsilane $(\text{CH}_3)_4\text{Si}$, 450° ; trimethylsilane $(\text{CH}_3)_3\text{SiH}$, 310° ; dimethylsilane $(\text{CH}_3)_2\text{SiH}_2$, 220° ; methylsilane CH_3SiH_3 , 130° ; and vinylsilane $\text{H}_2\text{C}=\text{CH}-\text{SiH}_3$, 90° .

2. Explosion temperatures of alkylsilanes were found to be lower than those of analogous hydrocarbon compounds which have explosion temperatures between 500° and 600°C .

CONCLUDING REMARKS

1. The large variation in explosion temperatures among the silanes indicates that substituting hydrogen atoms for the methyl groups decidedly increased their reactivity and may cause marked changes in the combustion properties among members of this class of fuels.

2. Since the explosion temperature is lower for the alkylsilanes than for the hydrocarbons and since it decreases as hydrogen atoms are substituted for methyl groups, the Si-H bond is probably more susceptible to oxidation than the C-H bond.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, November 25, 1953

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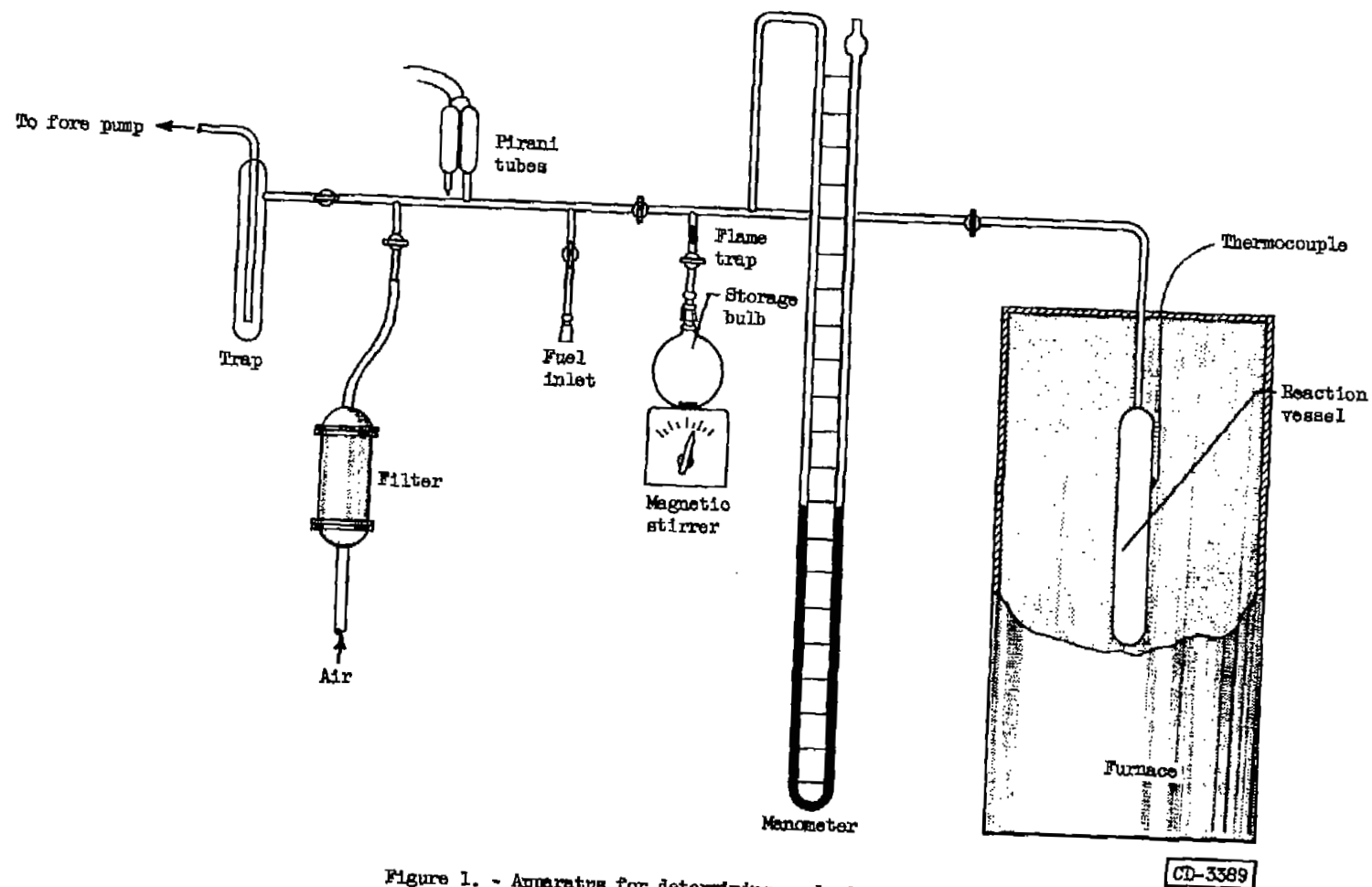


Figure 1. - Apparatus for determining explosion limits.

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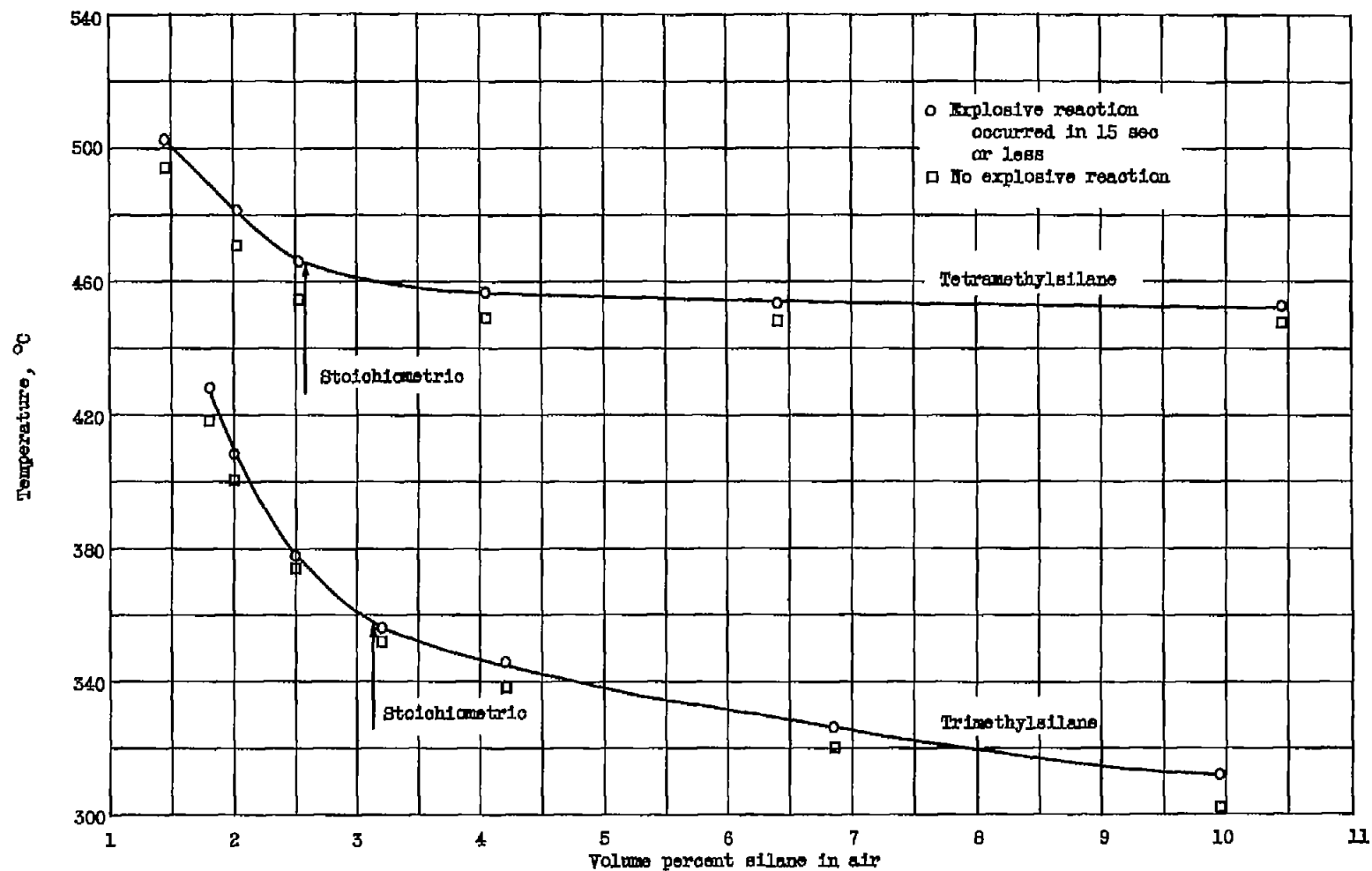


Figure 2. - Temperature-composition explosion curves for tetramethyl- and trimethylsilane at pressure of 1 atmosphere.

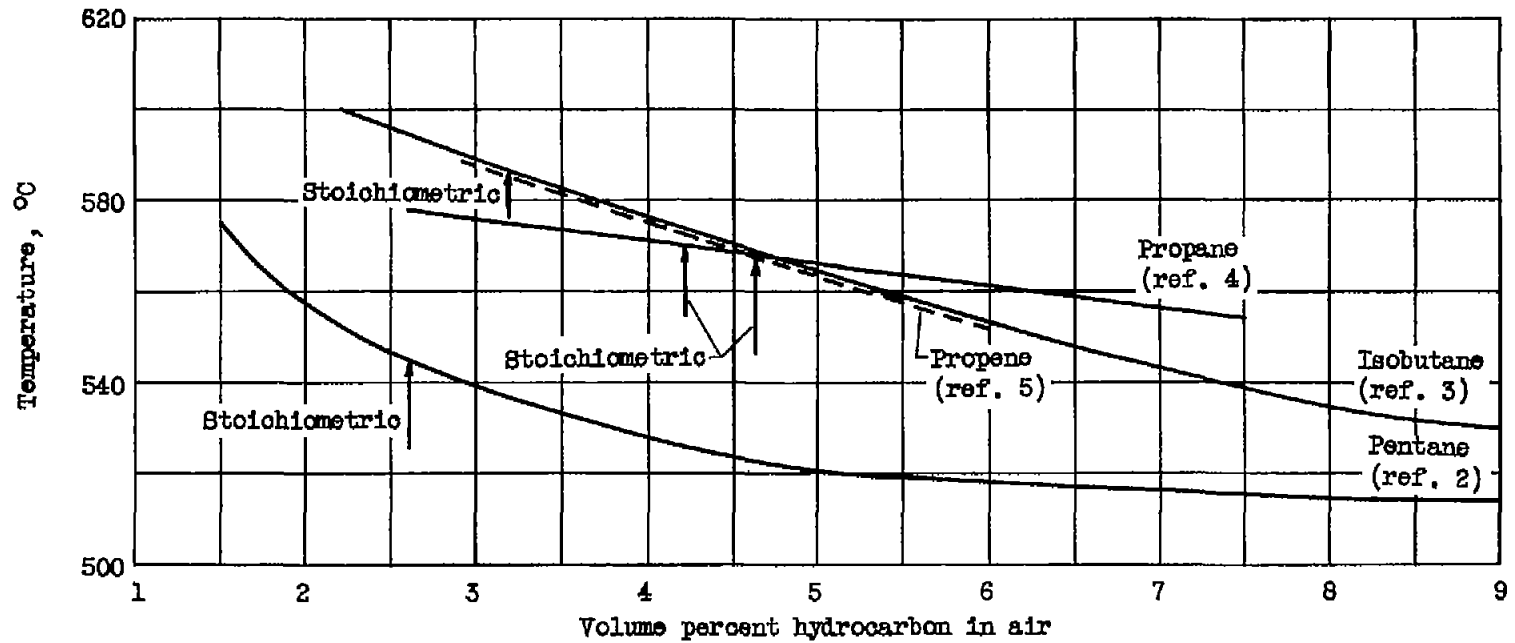


Figure 3. - Temperature-composition explosion curves for hydrocarbons at pressure of 1 atmosphere.

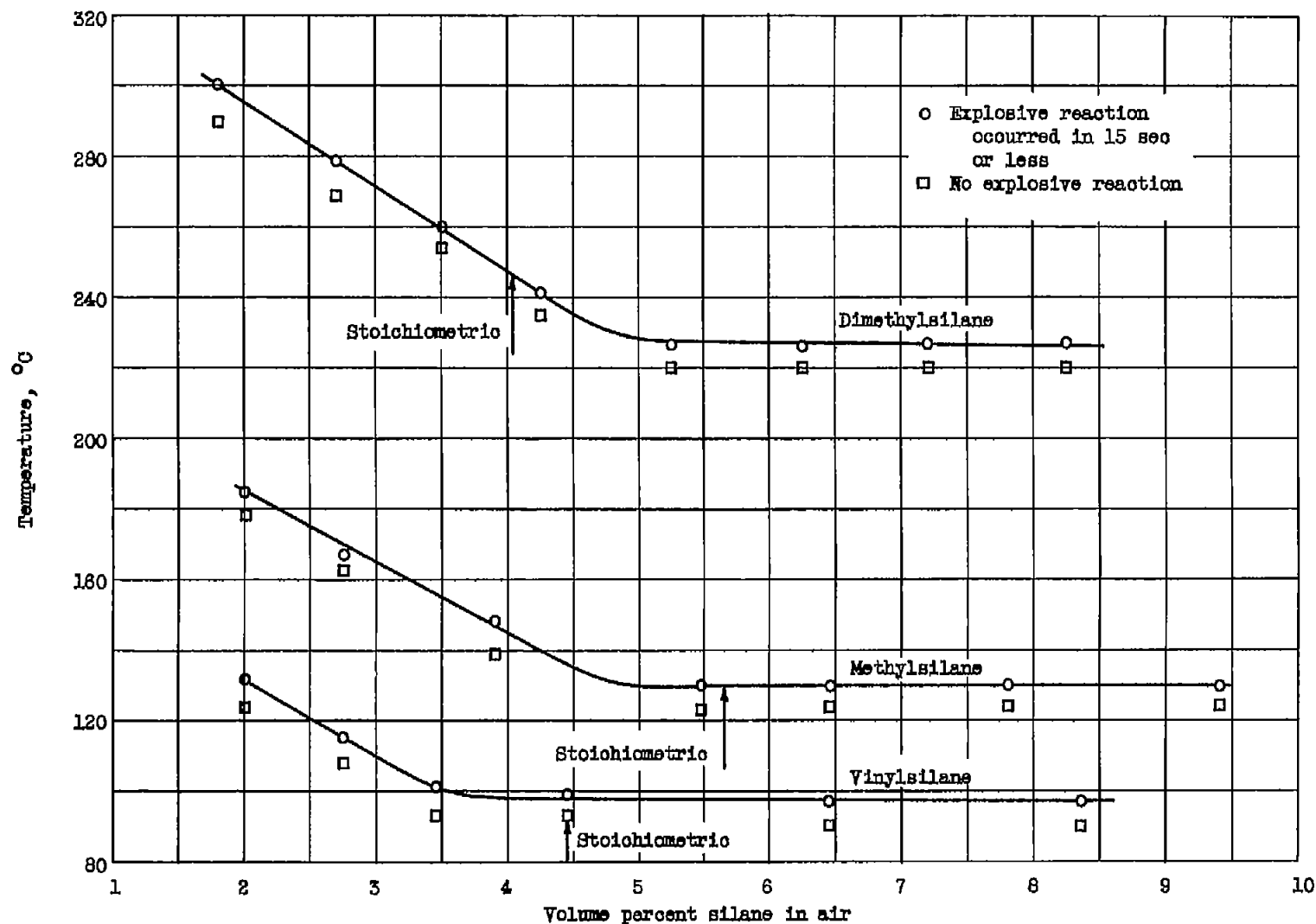


Figure 4. - Temperature-composition explosion curves for dimethyl-, methyl-, and vinylsilane at pressure of 1 atmosphere.

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